(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 624 400 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
10.09.1997 Bulletin 1997/37

(51) Int. Cl.[6]: B01J 23/94

(21) Application number: 94303329.0

(22) Date of filing: 09.05.1994

(54) Synthesis gas process with reactivation of catalyst

Verfahren zur Herstellung von Synthesegas mit Reaktivierung des Katalysators

Procédé de préparation de gaz de synthèse avec réactivation du catalyseur

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: 11.05.1993 US 60333

(43) Date of publication of application:
17.11.1994 Bulletin 1994/46

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(56) References cited:
EP-A- 0 135 729
GB-A- 1 455 030

EP 0 624 400 B1

Printed by Rank Xerox (UK) Business Services
2.14.12/3.4

Description

This invention relates to a pr cess for the production of synthesis gas employing a nickel-on-alpha alumina catalyst, which process includes the reactivation of the nickel-on-alpha alumina catalyst.

The production of synthesis gas, r syn gas (carbon monoxide and hydrogen) via the reaction of low molecular weight hydrocarbons, primarily m thane, within a fluidized bed of catalyst in the presence of steam (steam reforming process) or oxygen (partial oxidation process) is well known. Processes wherein the light hydrocarbons are converted to syn gas within a fluidized bed of catalyst, e.g., nickel on an alpha alumina support, at elevated temperatures in the presence of both steam and oxygen (air) are also well known, and this type of process may offer particular advantages in that the molar ratio of hydrogen and carbon monoxide can be better controlled to produce a gas particularly suitable for conducting Fischer-Tropsch reactions. In conducting Fischer-Tropsch operations, it is required that the molar ratio of the hydrogen:carbon monoxide used be maintained at about 2:1.

Fluidized bed processes offer particular advantages in that they provide superior heat and mass transfer characteristics as contrasted with fixed bed processes. Fluidized processes permit substantially isothermal reactor conditions in conducting both exothermic and endothermic reactions. However, there are certain problems inherent in fluidized bed operations, notable among which is the sensitivity of the process to changes in the catalyst produced during the operation. Agglomeration and sintering of the solid catalytic particles during high temperature reactions and/or the introduction of contaminating substances into the catalyst by the feed reduces the activity of the catalyst.

During the reaction the catalytic metal component, i.e., nickel, grows in crystallite size. The alumina particles also agglomerate to adversely affect the fluidization characteristics of the bed, and the activity of the catalyst declines. Contaminants, introduced into the fluidized bed, eliminate or shield catalyst sites with further reduction of catalytic activity. Relatively high methane in the syn gas product and the decline in catalyst activity during normal operations seriously debits the process, and sooner or later the deactivated catalyst must be regenerated or replaced by fresh catalyst.

Other processes which include a nickel catalyst regeneration step are known in EP-A-0 135 729 and GB-A-1 455 030. In the former document, the process disclosed is one of preparing methane-rich gases in a fixed bed of supported nickel catalyst. In the latter document, the process disclosed is one of selectively hydrogenating di-olefins and/or acetylenes, in the presence of mono-olefins, in a fixed bed of supported nickel catalyst. In each case, catalyst regeneration is conducted by first shutting down production and then regenerating the nickel catalyst in situ by burning off deposits. The catalyst is then reduced with hydrogen, after which the respective manufacturing process is started up again.

The present invention provides a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of nickel-on-alpha alumina catalyst at elevated temperature in the presence of steam and oxygen, in a reaction zone operated in a net reducing atmosphere, which process includes the steps of :

withdrawing a portion of said catalyst and contacting it with an oxygen-containing gas at a temperature of at least 705°C (1300°F) to convert the nickel component to nickel aluminate, and disperse said nickel aluminate within the alpha alumina support, without sintering said alpha alumina support; and

recycling said catalyst after contact with the oxygen-containing gas to the reaction zone to reduce therein the nickel aluminate component of the catalyst, and increase the activity of the catalyst vis-vis that of the catalyst initially withdrawn from the reaction zone.

In a preferred method of operation, the catalyst is classified according to particle size distributions, e.g., by elutriation from a fluidized bed, with or without the use of one or more cyclone separators, located above the bed, via the use of one or a series of cyclone separators used with a collection vessel, or by sieve separation means, and a preselected portion of the catalyst particles is withdrawn from the reactor, or reaction zone, and treated. The non-selected portion, or portions, of catalyst can be recycled, or discarded, as determined by process economics.

In a particularly preferred embodiment, an additional activity boost is provided to a contaminated nickel-on-alumina catalyst after oxidation of the nickel component of the catalyst with an oxygen-containing gas at elevated temperature to form nickel aluminate by treatment of the catalyst with an acid solution to remove contaminant surface impurities, without dissolving the nickel aluminate, prior to recycle of the catalyst to the reactor, or reaction zone. The oxidation treatment with an oxygen-containing gas thus increases the activity of the catalyst, on reduction, to a level above that of the catalyst initially withdrawn from the reactor, or reaction zone. The treatment with the acid solution further increases the activity of the catalyst, on reduction, to an even higher level; viz. to a level greater than that of the catalyst subjected to the oxidation treatment, and reduced. The activity of a nickel-on-alumina catalyst subjected to both the oxidation and acid treatments more closely approaches that of the fresh catalyst. Moreover, as a result of the decrease in the level of surface contaminants resultant from the acid treatment, the catalyst has less tendency to agglomerate when recycled to the bed of the syn gas reactor, or reaction zone.

This invention, and its principle of operation, will be more fully understood by reference to the following detailed description of specific and preferred embodiments, and to the attached drawings to which reference is made in the

description. In the different views, identical numbers are used to designate corresponding parts, or components.

R ference to the Drawings

Figure 1 graphically depicts, in flow diagram format, a preferred process for the practice of this invention. In this figure, the numeral 10 refers to the syn gas reactor, the numeral 20 refers to the high temperature oxidation zone wherein catalyst from the reactor is treated to obtain a first activity boost, and numeral 30 refers to a preferred catalyst size classification zone wherein catalyst withdrawn from the reactor can be classified in optimal particle size distributions for treatment. The whole of the catalyst, or catalyst of optimum particle size distribution, after oxidation treatment, is treated in said acid treat zone 40 to provide an additional activity boost. The numeral 50 refers to a catalyst filtration and drying zone.

Figures 2-4 schematically depict preferred catalyst classification means: Figure 2 depicting particle size classification via use of an elutriating fluid bed with internal cyclones; Figure 3 depicting classification of the particles based only on cyclone separators; and Figure 4 depicting particle size classification via sieve separation.

Detailed Description of the Invention

Referring first to Figure 1, synthesis gas is produced in fluidized bed reactor 10. Preheated light hydrocarbons, C_1-C_4 alkanes, predominantly methane, steam and oxygen or an oxygen-containing gas (air), are fed into reactor 10 via lines 11, 12, 13, respectively, and reacted within a fluidized bed of nickel-alpha alumina catalyst at temperatures above about 1500°F (816°C), preferably at temperatures ranging from about 1700°F (927°C) to about 1900°F (1038°C), sufficient to convert the hydrocarbon feed to hydrogen and carbon monoxide, or syn gas, without significant disintegration of the catalyst to fines, or catalyst agglomeration. Pressures range generally from about 1 to 40.5 bar (atmospheric to about 40 atmospheres), preferably from about 20.3 to 30.4 bar (20 atmospheres to about 30 atmospheres) where a 2:1 molar ratio of hydrogen:carbon monoxide is desirable for the production of Fischer-Tropsch synthesis gas, and the avoidance of interstage compression.

The catalyst of the fluidized bed is one which contains generally from about 1 percent to about 20 percent nickel, preferably from about 5 percent to about 10 percent nickel, composited with an alpha alumina support, based on the total weight of the catalyst. The fluidized bed may also contain, and generally does contain a particulate solids diluent to disperse heat, suitably high purity alpha alumina. Generally, the bed is constituted of from about 10 percent to about 99.9 percent, preferably from about 80 percent to about 99.5 percent, of the solid diluents component and from about 0.1 percent to about 90 percent, preferably from about 0.5 percent to about 20 percent, of the catalyst, based on the total weight of the particulate solids constituting the fluidized bed. A hydrogen and carbon monoxide product, steam, some unconverted hydrocarbons and other materials exit overhead line 14, cyclone separators 15, 16 trapping some of the catalyst particles and fines, returning them via their respective diplegs to the reactor. The mean average diameter of the particles constituting the fluidized bed generally ranges from about 30 microns to about 150 microns, the key fluidization characteristics determined by particle size distribution, e.g., bubble size, fluidization regime, being well known and understood by those skilled in this art.

In the initial step of reactivating, or regenerating, the catalyst a portion of the catalyst is withdrawn from the bottom of reactor 10 via line 17 and contacted in catalyst oxidation zone 20 with oxygen, or an oxygen-containing gas, preferably air, at temperature elevated sufficiently to convert the nickel or nickel oxide surface component, or components, of the catalyst to nickel aluminate and disperse said nickel aluminate component within the alumina support. The catalyst is contacted with the oxidizing gas, e.g., air, at a temperature of at least 1300°F (705°C), preferably at temperatures ranging from 1300°F (705°C) to 2400°F (1315°C), more preferably from 1600°F (870°C) to 2000°F (1093°C), for a period sufficient to convert the nickel, or nickel oxide component, to nickel aluminate without sintering the catalyst. Generally, at temperatures ranging from about 1600°F (871°C) to about 2000°F (1093°C) from about 0.1 hour to about 20 hours, or most often from about 0.5 hour to about 16 hours, are adequate to restructure, disperse and convert the nickel, or nickel oxide component of the catalyst to nickel aluminate. On withdrawal of the oxidized catalyst from oxidation zone 20, and recycle thereof via line 18 to the reactor 10, the nickel alumina component of the catalyst is reduced in the reducing atmosphere of the reactor to metallic nickel and the catalyst thereby reactivated. or rejuvenated.

Optionally, continuing the reference to Figure 1, instead of treating the whole of the catalyst withdrawn from reactor 10, the catalyst can be classified according to size in catalyst size classification zone 30 to reduce the quantity of the catalyst treated. This is advantageous because the nickel tends to concentrate in the coarse fraction, or fraction wherein the average particle size diameters are greater than about 90 microns. Suitably, a coarse fraction of average particle size diameters ranging between about 90 microns and 200 microns is selected for treatment. Thus, in a preferred embodiment only a selected portion of the catalyst withdrawn from the reactor 10 is treated in high temperature oxidation zone 20, while another portion, or portions, of the withdrawn solids is recycled without treatment via line 19 to th reactor 10. The classification of the withdrawn catalyst particles can be performed in various ways, suitably by elutriation from a fluidized bed, with or without the use of one or a series of cyclone separators located above the bed, via

the use of one or a series of cyclone separators mounted above a vessel that collects the coarse fraction of the catalytic solids, or via sieve separations as represented via "block 30" in Figure 1. Thus, with valve 31 closed, and valves 32, 33 pen, the whole of the catalys: withdrawn from reactor 10 via line 17 can be passed into catalyst classification zone 30 via line 34. The desired portion of catalyst can then be separated therefrom in zone 30, and then introduced via lines 35, 17 to the high temperatur oxidation zone 20. The residual, or non-selected portion of the catalyst can then be directly recycled via line 19 to the reactor 10.

Referring specifically to Figure 2 there is schematically depicted a fluid bed elutriator 30_1, or classifier which utilizes a vessel 9 which contains a pair of internal cyclones 2, 3 for selection of catalyst particles of desired size distributions for subsequent treatment. The cyclones 2, 3 are located within and above a fluidized bed 7 of the catalyst, and the latter is supported atop a grid 6. Fines particles are removed from the cyclones 2, 3 via line 19 located at the top of the vessel, and coarser particles are returned to the fluidized bed 7 via the diplegs of the cyclones. A slipstream of catalytic solids withdrawn via line 17 from the reactor 10, is thus fed via valved line 34 into the vessel 9 into the bottom of which heated gas, e.g., steam or air or both is introduced via line 8 to stratify the catalytic particles according to size, the coarser particles stratifying in the bottom portion of the fluidized bed, above the grid 6 near the bottom of the vessel. The coarser particles of preselected size are withdrawn from the bed via valved line 35 and fed, via line 17, into the high temperature oxidation zone 20. Fines particles are withdrawn from the vessel 30_1 via line 19 and recycled to the reactor, or further classified according to preselected particle size distributions via means not shown.

Reference is now made to Figure 3 which schematically depicts a cyclone (centrifugal) classification system 30_2 wherein cyclones 2^1, 3^1 are serially mounted externally and above the vessel 9^1 within the bottom of which is contained a bed 7^1 of catalytic solids particles. In the operation of this cyclone classification system, the slipstream of catalytic solids withdrawn via line 17 from the reactor 10 is thus fed via line 34 into the first cyclone 2^1 of the series, fines solids particles ascending and entering onto the top of the second cyclone 3^1 of the series, exiting via line 19^1. The coarser particles pass downwardly through the two diplegs of the cyclones, respectively, and enter into the bed 7^1 of the vessel 9^1. A coarse particulate solids fraction of preselected size is withdrawn via line 35 and fed, via line 17 into the high temperature oxidation zone 20.

Referring to Figure 4, there is also depicted a screen sieve classification system 30_3 which can also be employed for separation of a coarse particulate catalyst fraction from fines solids particles. In this figure, there is thus illustrated a trough shaped container, or vessel 51 across the upper side of which is located a sieve screen 52. Solids particles withdrawn from the reactor are thus fed via line 34 atop the screen 52, of preselected mesh size. Fines are passed through the screen 52 to enter into the vessel 51 from where they are removed via line 53. The coarser solids particles, which cannot pass through the screen 52, are passed via line 35 to the high temperature oxidation zone 20.

Treatment of the catalyst via high temperature oxidation in zone 20, and subsequent reduction of the catalyst in the reactor 10 provides a substantial catalyst activity boost. There are a number of sources from which the catalyst can become contaminated, e.g., from the feed during the reaction, the reactor or reactor system, the carrier for the catalyst itself, or the solids diluent used to disperse heat. Hence, the catalyst almost invariably contains metal contaminants, such as alkali metals, e.g., sodium, potassium, and the like, or other metals, e.g., iron, and the like, or non metal contaminants, e.g., silicon, and the like, which suppresses the activity of the catalyst sufficiently that treatment in oxidation zone 20 does not fully restore the activity of the catalyst. Removal of these contaminants after treatment in oxidation zone 20, can provide a second, additional catalyst activity boost on return of the catalyst to reactor 10. Some of these contaminants also increase the tendency of the catalyst to agglomerate; and hence their removal is also helpful in suppressing this tendency. Consequently, after treatment of the catalyst in oxidation zone 20 the catalyst is preferably contacted, or washed with an acid sufficient to dissolve and remove the contaminants from the catalyst without dissolving significant amounts of the nickel aluminates. The acid used must preferably also be one which will not form a residue, or introduce other contaminants.

Acids suitable for dissolving out the impurities without significant reaction with the nickel aluminate, or formation of a residue, are certain of the mineral acids, exemplary of which are nitric acid, nitrous acid, and the like, carboxylic acids, e.g., formic acid, acetic acid, citric acid, and the like, polycarboxylic acids, e.g., oxalic acid and the like, hydroxycarboxylic acids, e.g., lactic acid, and the like, fluorosubstituted carboxylic acids, e.g., trifluoroacetic acid and the like, amino acids, e.g., ethylenediaminotetracetic acid (EDTA) and the like, sulfonic acids and substituted sulfonic acids, e.g., trifluoromethanesulfonic acid and the like. Acids containing anionic or free halides, e.g., HCl, are generally to be avoided. Suitably, the acids are used in aqueous solutions in concentrations providing from about 0.01 molar to about 1.0 molar, preferably from about 0.03 molar to about 0.1 molar, solutions. Referring again to Figure 1, catalyst withdrawn from oxidation zone 20 is thus passed via line 36 to a quench zone (not shown) wherein the catalyst is contacted with water to reduce the temperature of the catalyst to about ambient temperatures, and the catalyst then transported to acid treat zone 40.

In acid treat zone 40 the catalyst is contacted with a dilute concentration of the acid for time sufficient to remove a substantial portion of the surface contaminants without reacting with and dissolving a significant amount of the nickel aluminate, and without forming a residue. Generally, treatment of the catalyst with a dilute aqueous acid solution, e.g., a 0.1 molar nitric acid solution, over a period ranging from about 0.01 hour to about 2 hours, preferably from about 0.05

hour to about 0.5 hour, will remove a major part of the surface contaminants without reaction with the nickel aluminate component of the catalyst, and without formation of a residue. The acid treated catalyst is then removed from acid treat zone 40 via line 37 and introduced into filtration and drying zone 50. Within filtration and drying zone 50 th catalyst is separated from the acid solution, washed with water, suitably by filtration, hydroclone, or continuous centrifugation, and the wet catalyst then dried, .g., on a belt fed dryer, spray dryer, fluid bed dryer or the like. The dry catalyst is withdrawn from filtration and drying zone 50 and passed via lines 38, 18 to reactor 10.

The invention will be better understood via the following illustrative examples, which serve to demonstrate specific and preferred embodiments.

Example 1

A feed gas admixture in molar ratio of methane:water:oxygen of 1.0:0.5:0.5 is fed into a reactor employing a fluidized bed of nickel-on-alpha alumina catalyst, the nickel being dispersed on the catalyst in concentration of 8 percent nickel, measured as metallic nickel based on the weight of the catalyst. The catalyst is diluted with alpha alumina heat transfer solids particles such that the metallic nickel concentration, based on the weight of the bed, is about 0.3 weight percent. The reaction is conducted in a pilot plant unit at a nominal temperature of 1800°F (983°C) and 2.482 MPa (360 psia) to produce a synthesis gas containing approximately 2.72 mole % unreacted methane, 55.78 mole % hydrogen, 23.71 mole % carbon monoxide, 3.69 mole % carbon dioxide, and 14.10 mole % water.

After several days of operation, a slipstream withdrawn from the bottom of the reactor contains catalyst of average size diameter particle size distribution as follows:

>90 microns	9 wt%
75/90 microns	20 wt%
63/75 microns	31 wt%
53/63 microns	24 wt%
38/53 microns	14 wt%
<38 microns	2 wt%

A portion of the catalyst of size diameters greater than 90 microns is fed into a high temperature oxidation zone wherein the catalyst is contacted with air at 1800° F (983° C), at contact time sufficient to convert essentially all of the nickel component of the catalyst to nickel aluminate.

When a spent portion of catalyst is oxidized in this manner, and again employed in a reactor to convert the feed to syn gas it is found that the activity of the catalyst can be increased generally by an amount ranging from at least about 20% to 100%, based on the activity of the catalyst as withdrawn from the reactor. The following Examples 2 and 3 are exemplary of spent catalysts taken from a large pilot plant unit and oxidized, and reactivated, at different sets of conditions to provide increased activities ranging from about 24% to 96% vis-a-vis the deactivated catalysts.

Example 2

This example demonstrates the reactivation of a spent catalyst by high temperature oxidation. The catalyst employed in conducting these runs was a sample of bed material from a large synthesis gas pilot unit. The activity of the catalyst was measured in a fixed bed laboratory reactor system, a ceramic lined reactor designed to avoid mass and heat transfer limitations and provided with a rapid quench to avoid back reactions. Measurements were taken at 1800° F (983°C) and nominally 2.482 MPa (360 psia) with a feed mixture of CH_4:CO:H_2:H_2O equal to 1:1:1:2 and with a gas residence time of about 80 msec. The activity of the spent catalyst and this catalyst reactivated by air oxidation at 1400°F (760°C) for 16 hours (Reactivation 1) and 1800°F (983°C) for 16 hours (Reactivation 2) are shown in Table 1.

TABLE 1

Catalyst Reactivated by Oxidation			
Catalyst Sample	Oxidation Temperature, °F	Activity at 40 hrs, 1/sec	Activity at Increase, %
Spent Catalyst	(Base Case)	4.6	(Base Case)
Reactivation 1	1400 (760°C)	5.7	24
Reactivation 2	1800 (983°C)	9.0	96

Thus, as shown by the data, Reactivation 1 (1400°F; 760°C) gave an activity increase of 24% and Reactivation 2 (1800°F; 983°C) gave an activity increase of 96%.

Example 3

This example also shows the reactivation of a spent catalyst by high temperature oxidation. The catalyst is a sample of bed material from a large synthesis gas pilot unit but from a different time period from that used in Example 2. The steam reforming activity was measured in the laboratory reactor system described in Example 2. The activities of the spent catalyst and the catalyst reactivated by air oxidation at 870°C (1600°F) for 3 hours are shown in Table 2.

TABLE 2

Catalyst Reactivated by Oxidation			
Catalyst Sample	Oxidation Temp./Time	Activity at 40 hrs, 1/sec	Activity at Increase, %
Spent Catalyst	(Base Case)	13.2	(Base Case)
Reactivated	870°C (1600°F)/3 Hrs	17.1	30

Thus, as demonstrated, the reactivation at 1600°F (870°C) for 3 hours gave an activity increase of 30%.

The following exemplify the effect of acid washing to reduce the tendency of the catalytic particles to agglomerate due to the presence of surface contamination.

Example 4

Samples of a tabular alumina with a particle size range of 45-106 µm (150/325 mesh) were treated with dilute nitric acid solutions in variable concentration. The experiments were conducted by slurrying about 25 grams of the alumina powder in 200 cc of acid solution at room temperature for a period of 20 to 30 minutes using a magnetic stirrer to provide continuous agitation. After acid treatment, the alumina samples were collected in a small Buchner funnel and briefly rinsed with about 30-50 cc of deionized water. A control experiment was also carried out using water in place of nitric acid. After filtration, the alumina samples were dried at room temperature and then dried overnight in a vacuum oven maintained at 100°C.

The acid washed materials were tested for agglomeration resistance in a small fixed bed sintering test that has been developed to assess the agglomeration resistance of particulate oxides in fluid bed syn gas generation. In this test, an 8-10 gram sample of the particulate oxide was distributed in a small Coors alumina boat. The sample was placed in a high temperature Lindberg furnace and heated from room temperature to 1600°C over a period of about 90 minutes. The sample was then held at 1600°C for a period of 2 hours to induce thermal sintering and agglomeration. The sample was then cooled to about 100°C over a period of 6-12 hours and removed from the oven. The sample was then transferred to a sonic sieve operated at a constant power level, and the conversion of 45 to 106 µm particles to fused aggregates greater than 106 µm in size was determined by weighing the fractions collected on a 150 mesh size screen.

Table 3 compares agglomeration results for the tabular alumina materials treated with nitric acid at variable concentrations. It is easily seen that very dilute, 0.001 M nitric acid and/or washing with deionized water had little or no measurable impact on agglomeration resistance. However, treatment with more concentrated nitric acid solutions resulted in

significant improvements in agglomeration resistance. Samples treated with acid concentrations in the range of 0.1 to 0.5 M showed noticeably reduced agglomeration.

TABLE 3

Agglomeration Test Data and Surface Composition Results For Acid Treated Tabular Alumina					
Acid Washing Conditions	Agglomeration at 1600°C (% + 106 μm)	-------XPS Atomic Ratios -------			
		(NaAal)	(Ca/Al)	(Si/Al)	(B/Al)
None (Unwashed Standard)	47	0.10	0.012	0.034	0.046
None (Water Washed Blank)	44	0.12	0.012	0.034	0.051
0.001 M HNO_3	59	0.077	0.014	0.035	0.040
0.01 M HNO_3	16	0.059	0.009	0.021	0.035
0.1 M HNO_3	14	0.039	0.009	0.020	0.032
0.5 M HNO_3	11	0.014	0.009	0.016	0.009

Example 5

The surface composition of the materials considered in Example 4 was investigated using X-ray photoelectron spectroscopy in a conventional instrument manufactured by Leybold-Heraeus that employs that employs an Al-anode X-ray source. The surface atomic ratios of various impurity elements relative to aluminum were calculated by correcting the measured boron(1s), silicon(2s), sodium(1s), calcium(2p), and aluminum(2s) XPS peak areas with Scofield photo-ionization cross sections. Table 3 includes these atomic ratios for the materials studied. It can easily be seen that the acid washed materials with improved agglomeration resistance displayed reduced surface concentrations of impurity species. Boron, calcium, silicon, and sodium, in particular, were reduced to low levels after treatment with 0.1-0.5 M nitric acid.

Example 6

This example shows the reactivation of a spent catalyst by high temperature oxidation followed by an acid wash. The catalyst is a sample of bed material from a large synthesis gas pilot unit but from a different time period from that used in Examples 2 and 3. The steam reforming activity was measured in the laboratory reactor system described in Example 2. Table 4 shows the activities of the spent catalyst, the catalyst reactivated by air oxidation at 1800°F (983°C) for 16 hours and the catalyst reactivated by the oxidation followed by an acid wash in either 0.1 M (molar) or 1.0 M nitric acid for 20 minutes.

TABLE 4

Catalyst Reactivation by Oxidation Plus Acid Wash				
Catalyst Sample	Oxidation Temperature/Time	Acid Wash Conc./Time	Activity At 40 Hrs, 1/Sec	Activity Increase, %
Spent Catalyst	(Base Case)	--	16.4	(Base Case)
Oxidation	983°C (1800°F)/16 Hrs.	--	23.5	43
Oxidation + Acid Wash	983°C (1800°F)/16 Hrs.	0.1 M/20 Min.	28.3	73
Oxidation + Acid Wash	983°C (1800°F)/16 Hrs.	1.0 M/20 Min.	31.1	90

As shown in Table 4, the reactivation by air oxidation gave an activity increase of 43%, and the oxidation followed by an acid wash gave an additional activity increase to 73% with the 0.1 M nitric acid wash and an additional activity increase to 90% with the 1.0 M nitric acid wash.

Claims

1. A process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of nickel-on-alpha alumina catalyst at elevated temperature in the presence of steam and oxygen, in a reaction zone operated in a net reducing atmosphere, which process includes the steps of :

   withdrawing a portion of said catalyst and contacting it with an oxygen-containing gas at a temperature of at least 705°C (1300°F) to convert the nickel component to nickel aluminate, and disperse said nickel aluminate within the alpha alumina support, without sintering said alpha alumina support; and

   recycling said catalyst after contact with the oxygen-containing gas to the reaction zone to reduce therein the nickel aluminate component of the catalyst, and increase the activity of the catalyst vis-a-vis that of the catalyst initially withdrawn from the reaction zone.

2. The process of Claim 1, wherein the temperature of treatment ranges from 705°C (1300°F) to 1315°C (2400°F).

3. The process of Claim 2, wherein the temperature of treatment ranges from 870°C (1600°F) to 1090°C (2000°F).

4. The process of any preceding claim, wherein the nickel-on-alpha alumina catalyst withdrawn from the reaction zone is classified according to particle size distributions and divided into fractions, only one or some of the factions being treated by contact with the oxygen-containing gas.

5. The process of any preceding claim, wherein the portion of catalyst that is withdrawn from the reaction zone contains contaminants and the portion, or selected fraction(s) is treated, after contact with the oxygen-containing gas and prior to recycle, with an acid solution sufficient to dissolve and remove contaminants from the surface of the catalyst, without dissolving the nickel aluminate, to decrease the tendency of the catalyst to agglomerate on recycle of the catalyst to the reaction zone and to further increase the activity of the catalyst vis-a-vis that of the catalyst treated by contact with the oxygen-containing gas.

6. The process of Claim 5, wherein the acid employed is one which does not form a residue.

7. The process of Claim 5, wherein the acid is one or more selected from nitric acid, nitrous acid, carboxylic acids, inclusive of polycarboxylic acids, hydroxycarboxylic acids, fluorocarboxylic acids and the like, ethylenediaminotetracetic acid and sulfonic acids.

8. The process of any one of Claims 5 to 7, wherein the acid solutions are of concentrations ranging from 0.01 molar to 1.0 molar.

9. The process of any one ot Claims 5 to 7, wherein the catalyst, after treatment with the acid solution, is separated from the acid solution and dried.

Patentansprüche

1. Verfahren zur Herstellung von Wasserstoff und Kohlenmonoxid aus einem Kohlenwasserstoff mit niedrigem Molekulargewicht durch Kontakt mit einem Wirbelbett aus Nickel-auf-α-Aluminiumoxid-Katalysator bei erhöhter Temperatur in Gegenwart von Wasserdampf und Sauerstoff in einer in einer netto reduzierenden Atmosphäre betriebenen Reaktionszone, bei dem

   ein Teil des Katalysators abgezogen und mit einem sauerstoffhaltigen Gas bei einer Temperatur von mindestens 705°C (1300°F) kontaktiert wird, um die Nickelkomponente in Nickelaluminat umzuwandeln und das Nickelaluminat in dem α-Aluminiumoxidträger zu dispergieren, ohne den α-Aluminiumoxidträger zu sintern, und der Katalysator nach Kontakt mit dem sauerstoffhaltigen Gas zu der Reaktionszone zurückgeführt wird, um darin die Nickelaluminatkomponente des Katalysators zu reduzieren und die Aktivität des Katalysators gegenüber der des anfangs aus der Reaktionszone abgezogenen Katalysators zu erhöhen.

2. Verfahren nach Anspruch 1, bei dem die Behandlungstemperatur im Bereich von 705°C (1300°F) bis 1315°C (2400°F) liegt.

3. Verfahren nach Anspruch 2, bei dem die Behandlungstemperatur im Bereich von 870°C (1600°F) bis 1090°C (2000°F) liegt.

4. Verfahren nach einem der vorhergehenden Ansprüche, bei dem der aus der Reaktionszone abgezogene Nickel-auf-α-Aluminiumoxid-Katalysator gemäß den Teilchengrößenverteilungen klassiert und in Fraktionen geteilt wird, wobei nur eine oder einige der Fraktionen durch Kontakt mit dem sauerstoffhaltigen Gas behandelt werden.

5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem der Teil des Katalysators, der aus der Reaktionszone abgezogen wird, Verunreinigungen enthält und dieser Teil oder eine ausgewählte Fraktion oder ausgewählte Fraktionen nach Kontakt mit dem sauerstoffhaltigen Gas und vor der Rückführung mit einer Säurelösung behandelt wird bzw. werden, die ausreicht, um Verunreinigungen von der Oberfläche des Katalysators aufzulösen und zu entfernen, ohne das Nickelaluminat aufzulösen, um die Neigung des Katalysators zum Agglomerieren bei Rückführung des Katalysators in die Reaktionszone zu verringern und die Aktivität des Katalysators gegenüber der des Katalysators, der durch Kontakt mit dem sauerstoffhaltigen Gas behandelt wurde, weiter zu erhöhen.

6. Verfahren nach Anspruch 5, bei dem die verwendete Säure keinen Rückstand bildet.

7. Verfahren nach Anspruch 5, bei dem die Säure eine oder mehrere ausgewählt aus Salpetersäure, salpetriger Säure, Carbonsäuren einschließlich Polycarbonsäuren, Hydroxycarbonsäuren, Fluorcarbonsäuren und dergleichen, Ethylendiaminotetraessigsäure und Sulfonsäuren ist.

8. Verfahren nach einem der Ansprüche 5 bis 7, bei dem die Säurelösungen Konzentrationen im Bereich von 0,01 molar bis 1,0 molar aufweisen.

9. Verfahren nach einem der Ansprüche 5 bis 7, bei dem der Katalysator nach Behandlung mit der Säurelösung von der Säurelösung abgetrennt und getrocknet wird.

Revendications

1. Procédé de production d'hydrogène et de monoxyde de carbone à partir d'un hydrocarbure de faible poids moléculaire par mise en contact avec un lit fluidisé de catalyseur de nickel sur alpha-alumine à température élevée en présence de vapeur d'eau et d'oxygène, dans une zone réactionnelle opérant dans une atmosphère nettement réductrice, ledit procédé comprenant les étapes suivantes:

    on retire une partie dudit catalyseur et on la met en contact avec un gaz contenant de l'oxygène à une température d'au moins 705°C (1300°F) pour convertir le constituant de nickel en aluminate de nickel et disperser ledit aluminate de nickel dans le support d'alpha-alumine, sans fritter ledit support d'alpha-alumine, et
    on recycle ledit catalyseur après contact avec le gaz contenant de l'oxygène dans la zone réactionnelle pour y réduire le constituant d'aluminate de nickel du catalyseur et augmenter l'activité du catalyseur vis-à-vis de celle du catalyseur initialement retiré de la zone réactionnelle.

2. Procédé selon la revendication 1, dans lequel la température de traitement se situe dans une plage de 705°C (1300°F) à 1315°C (2400°F).

3. Procédé selon la revendication 2, dans lequel la température de traitement se situe dans une plage de 870°C (1600°F) à 1090°C (2000°F).

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur de nickel sur alpha-alumine retiré de la zone réactionnelle est classifié en fonction de distributions de la granulométrie et divisé en fractions, une seulement ou quelques unes des fractions étant traitées par mise en contact avec le gaz contenant de l'oxygène.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la partie du catalyseur qui est retirée de la zone réactionnelle contient des contaminants et on traite la partie, ou des fractions sélectionnées, après mise en contact avec le gaz contenant de l'oxygène et avant le recyclage, avec une solution d'acide suffisante pour dissoudre et éliminer les contaminants de la surface du catalyseur, sans dissoudre l'aluminate de nickel, pour réduire

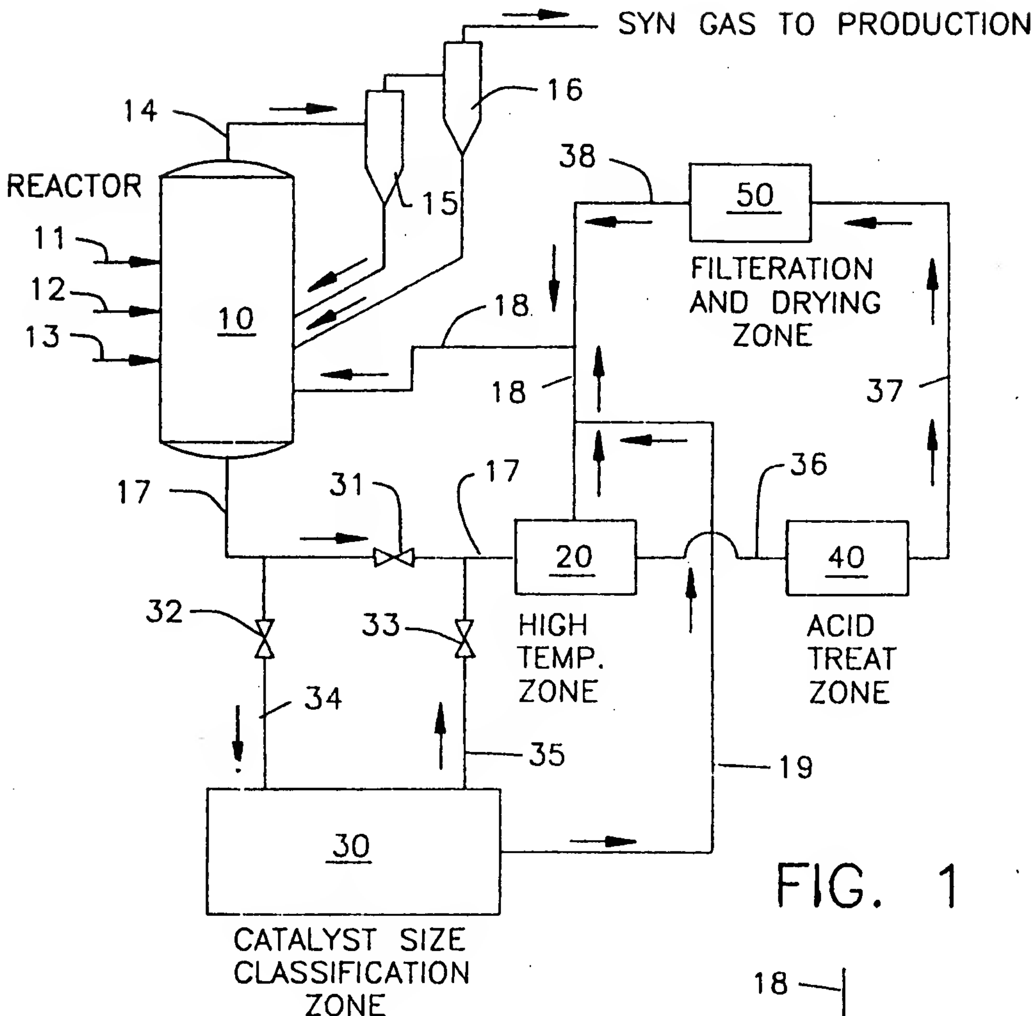
la tendance du catalyseur à s'agglomérer lors du recyclage du catalyseur dans la zone réactionnelle et pour encore augmenter l'activité du catalyseur vis-à-vis de celle du catalyseur traité par mise en contact avec le gaz contenant de l'oxygène.

6. Procédé selon la revendication 5, dans lequel l'acide utilisé est un acide qui ne forme pas de résidu.

7. Procédé selon la revendication 5, dans lequel l'acide est constitué d'un ou plusieurs acides sélectionnés parmi l'acide nitrique, l'acide nitreux, les acides carboxyliques, y compris les acides polycarboxyliques, les acides hydroxycarboxyliques, les acides fluorocarboxyliques, etc., l'acide éthylènediaminotétracétique et les acides sulfoniques.

8. Procédé selon l'une quelconque des revendications 5 à 7, dans lequel les solutions d'acide ont des concentrations dans la plage de 0,01 mole à 1,0 mole.

9. Procédé selon l'une quelconque des revendications 5 à 7, dans lequel le catalyseur, après traitement avec la solution d'acide, est séparé de la solution d'acide et séché.


SYN GAS TO PRODUCTION
16
14
15
REACTOR
10
11
12
13
38
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FILTERATION AND DRYING ZONE
18
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17
31
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HIGH TEMP. ZONE
ACID TREAT ZONE
34
35
19
30
CATALYST SIZE CLASSIFICATION ZONE

FIG. 1

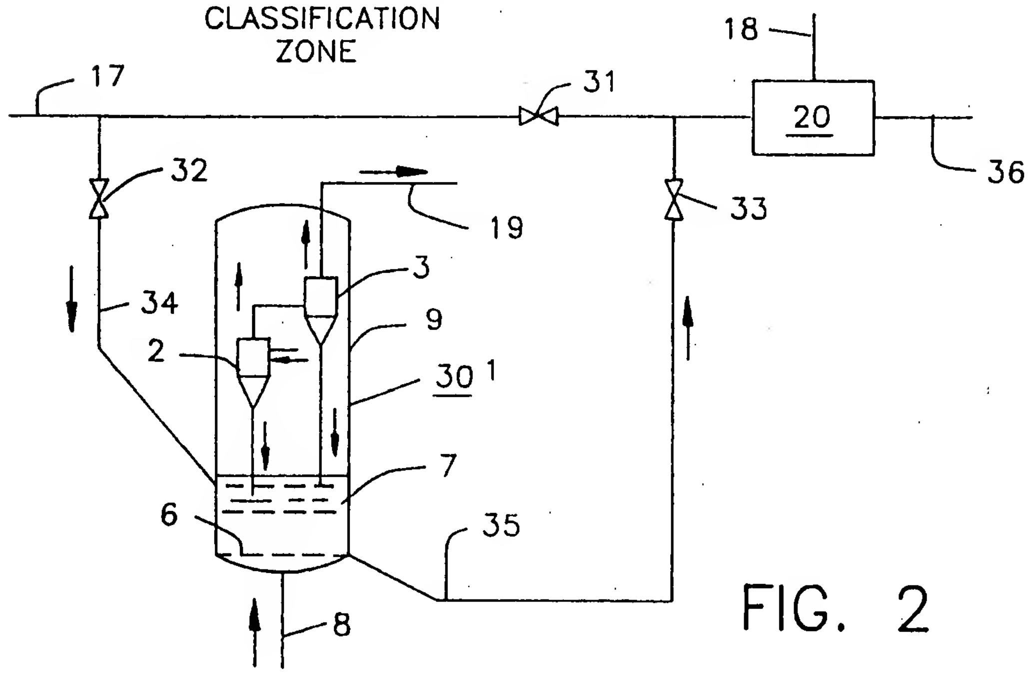
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FIG. 2

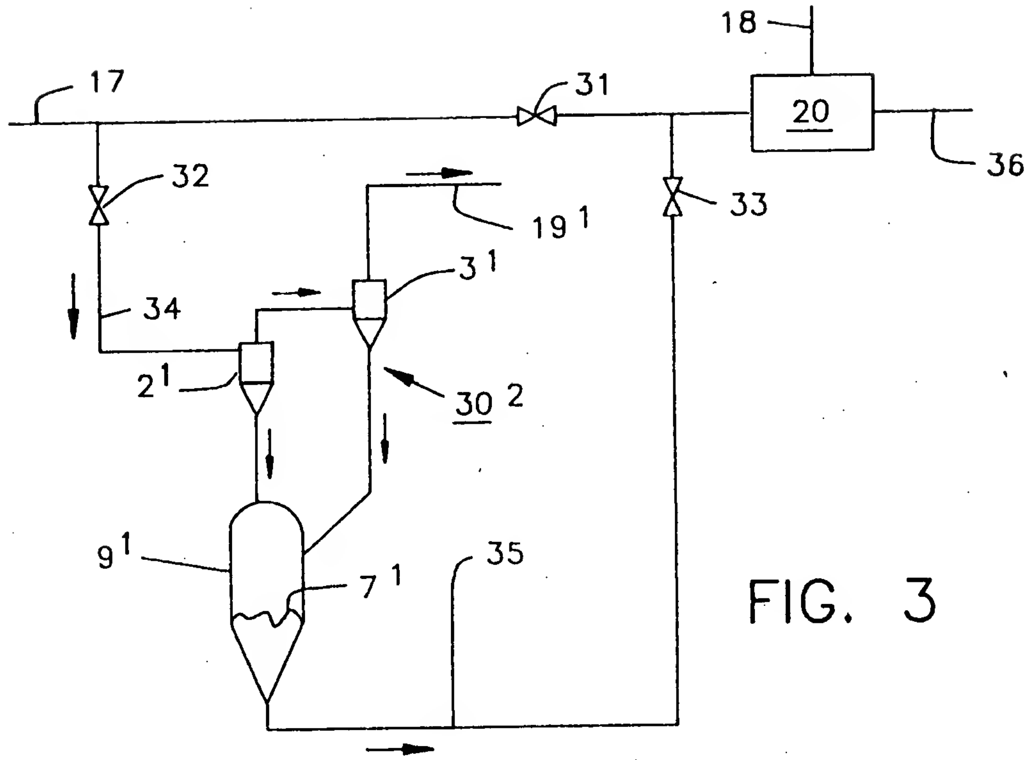
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FIG. 3

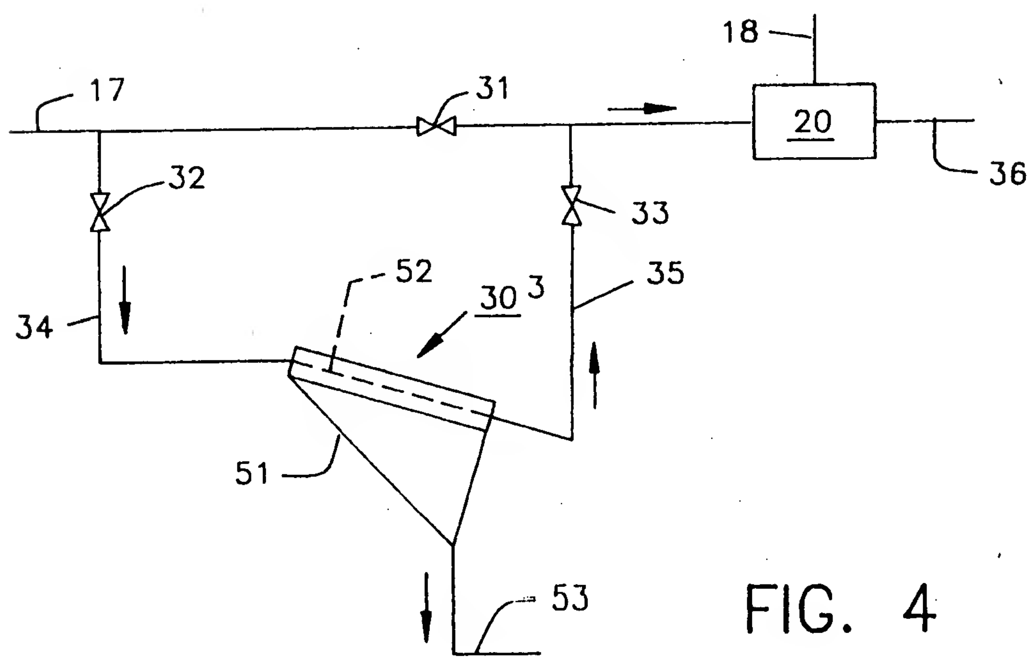
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FIG. 4